Quantitative Chemical Mass Transfer in Coastal Sediments During Early Diagenesis: Effects of Biological Transport, Mineralogy, and Fabric

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LONG-TERM GOAL

The long-term goal is to develop a better mechanistic and quantitative understanding of the effects of biologically-enhanced transport, sediment fabric, and particle surface chemistry on the biogeochemical dynamics of coastal marine sediments.

OBJECTIVES

The objectives for FY99 were (1) to quantify the solute transport processes in cohesive coastal sediments as functions of depth-dependent burrow distribution, ratio of active to abandoned burrows, and burrow flushing frequencies; and (2) to acquire and refine submicron-scale tools to investigate the relationship between organic matter (OM) reactivity and fabric parameters. The short-term goals included (1) continued bimonthly sampling, analyses, and data syntheses of St. Louis Bay and Horn Island test sites; (2) designing, establishment, sampling, analyses, and data syntheses of benthic mesocosm tank experiments; (3) quantitative description of biologically-enhanced solute transport (i.e., bioirrigation) in the field and laboratory sediments that explicitly considers depth-dependent burrow distribution, ratio of active to abandoned burrows, and burrow flushing frequencies; and (4) 10-50 nm scale carbon mapping using energy-filtering transmission electron microscopy (EFTEM) to investigate the spatial relationship between clay mineral particles and sedimentary OM.

APPROACH

My technical approach for the bioirrigation study was to analyze the spatial and temporal distribution of intrinsic solute tracers (NH_4, PO_4, SO_4, and TCO_2, using standard methods of spectrophotometry, ion chromatography, and potentiometric titration) in conjunction with the depth-dependent burrow distribution (by X-radiography), ratio of active to abandoned burrows (by X-radiography and animal counts), and burrow flushing frequencies (by visual observations of flushing events aided by the use of deliberate solute tracers). Sediments from the benthic mesocosm tanks were characterized for all parameters listed above. Sediments from the field test sites were characterized for all parameters listed above except the burrow flushing frequencies. *Schizocardium* sp. was used in the tank experiments as the bioirrigator of choice, as it was found to be adaptable to the tank environment and to be a rigorous bioirrigator that flushes its U- or V-shaped burrows in one direction. The data were used to write and test a solute transport model in which depth-dependent burrow distribution, ratio of active to abandoned burrows, and burrow flushing frequencies were explicitly considered. Designing, establishing, and sampling of the benthic mesocosm tank experiments were a collaborative effort

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among Sam Bentley (LSU), Dawn Lavoie (NRL), and myself. Characterization of burrow flushing included contributions by Philippe Van Cappellen (U. Utrecht) and Carla Koretsky (GA Tech).

My technical approach for the OM mapping was to image the distribution of carbon within clay aggregate samples from St. Louis Bay and benthic mesocosm tanks using EFTEM. EFTEM has an advantage over the traditional staining techniques for the OM visualization because the investigators do not have to rely on the assumption that all sedimentary OM has the recognizable morphological features. Thus, EFTEM allows to unveil OM that does not exhibit well-studied features such as polysaccharide webs and cell structures. Epoxy resin, a common embedding medium for the preparation of sedimentary samples for electron microscopy, is a carbon compound and would interfere with the mapping of intrinsic organic carbon. Consequently, I chose to use amorphous elemental sulfur as the embedding medium.

WORK COMPLETED

One set of benthic mesocosm experiments, in which two separate tanks were populated with 800 and 96 individuals/m^2 of *Schizocardium* sp., ran for over three months and was completed. The analyses included animal counts, burrow geometry and distributions, spatial distribution of solute species, and burrow flushing frequency. The second set of experiments, in which four tanks are each populated with 800 individuals/m^2 *Schizocardium* sp., has been running for six months.

Four trips to St. Louis Bay test site and two trips to Horn Island test site were completed along with the analyses of the spatial distribution of solute species, burrow geometry and distributions, and animal counts.

A numerical model for bioirrigation was formulated using the benthic mesocosm data. The model explicitly utilizes information on depth-dependent burrow distribution, ratio of active to abandoned burrows, and burrow flushing frequencies. The model is being applied to data from St. Louis Bay and Horn Island.

Spatial mapping of organic carbon in 10-50 nm scale using EFTEM has been completed for clay-OM aggregate samples from St. Louis Bay. The mapping technique has also been utilized to analyze matrix, fecal mounds, and burrow wall samples from the benthic mesocosms.

RESULTS

Depth-dependent distribution of burrows---Using X-radiography, The depth-dependent distributions of burrows in the experimental tanks were determined as shown in Figure 1a.

Burrow flushing frequencies---Each observed burrow occupied by *Schizocardium* sp. was found to be flushed every 20 to 120 seconds. Assuming a complete replacement of burrow water by the overlaying oxygenated water, this frequency of exchange allows the burrow water chemistry to stay virtually identical to the overlaying water, as found in the modeling work by Boudreau and Marinelli (1994).

Ratio of active to abandoned burrows---The number of burrows determined from X-radiography was compared to the number of animals introduced to each experimental tank, showing that 33 % of all burrows were occupied at the time of X-radiography sampling. The irrigation coefficient determined using the number of burrows needs to be adjusted accordingly.

Irrigation model---A numerical irrigation model based on the tube model (Aller, 1980) was developed. The present model is similar to the tube model as (1) it considers burrows as cylindrical void spaces that are filled with the water whose chemistry is equal to that of overlaying water and (2) it considers sediment to be composed of equally-spaced cylindrical microenvironments whose centers are occupied by the cylindrical voids. The solute transport in the sediments is calculated as the sum of vertical transport perpendicular to the water-sediment interface and radial transport perpendicular to the burrow walls. The present model is different from the tube model as the radius of microenvironment increases with depth reflecting the fact that the number of cylindrical voids participating in the radial diffusion transport decreases with depth. This allows the actual burrow counts from experimental tanks and field exercises to be explicitly incorporated into the model calculations. The SO_4^{2-} profiles calculated for both tanks using the actual depth-dependent burrow numbers shown in Figure 1a are shown in Figure 1b. The measured profiles are shown for comparison.

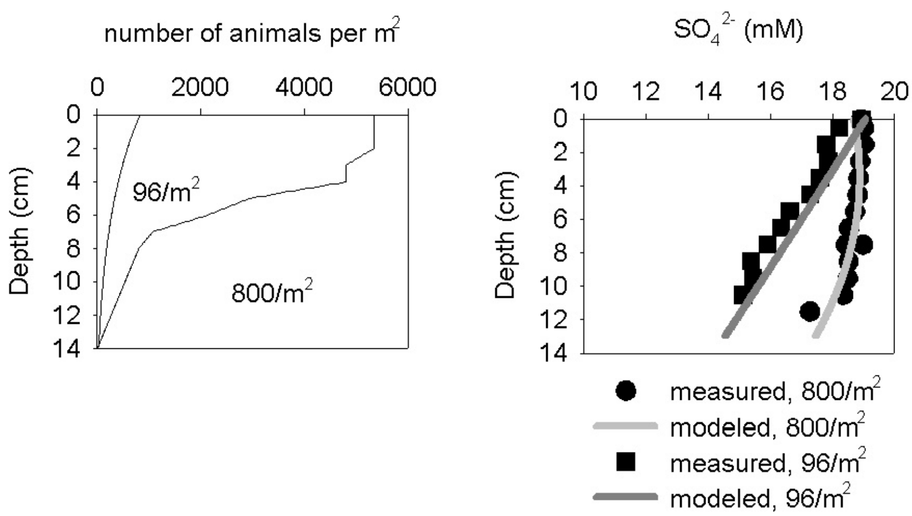

Figure 1a. Measured depth-dependent burrow density.
Figure 1b. Depth profiles of SO_4^{2-} in two experimental tanks.
Both measured and modeled profiles are shown.

OM imaging---EFTEM mapping of St. Louis Bay OM showed that OM has an intimate spatial relationship with clay aggregates. A typical clay mineral particle in a St. Louis Bay aggregate is very small (10-50 nm) and consequently the pore spaces associated with the aggregate is also 10-50 nm. OM in these aggregates exists within the intra-aggregate pore spaces, rather than as envelops around the aggregates. An example EFTEM image is shown in Figure 2.

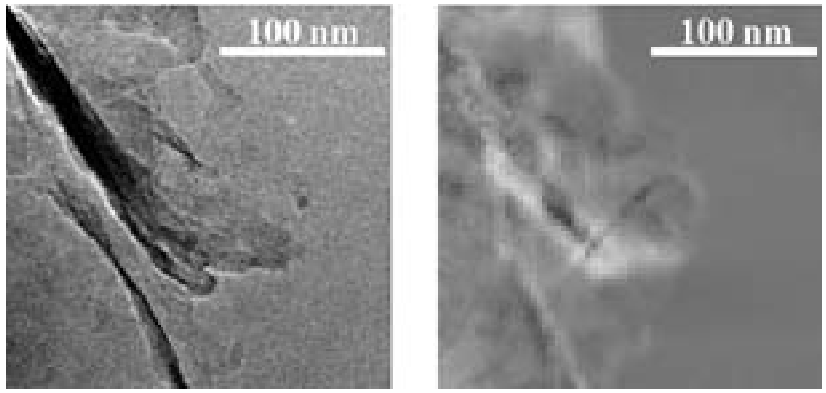

Figure 2.

Figure 2. Bright-field (left) and energy-filtering (right) images of a clay domain. In the EFTEM image, bright (white) areas represent locations where carbon signals significantly exceeded the background signals. Side-by-side comparisons of the bright-field and EFTEM images reveal the intimate spatial associations between individual clay plates and organic matter. The < 50 nm scale platy orientation seen in the bright field image due to the stacking of clay plates and pore spaces are also seen in the EFTEM carbon map.

IMPACT/APPLICATION

The simultaneous explicit parameterizations of burrow flushing frequencies, ratio of active to abandoned burrows, and spatial distribution of burrows will advance the community's understanding of bioirrigation. By applying the bioirrigation model to field sites, one can extract information on burrow flushing habits of organisms that are specific to each test site, which are difficult to measure in field environments yet important for the use of organisms for bioremediation. Treatment of bioirrigation in comprehensive reactive transport models for early diagenesis will be improved as a result of this study.

The EFTEM mapping of sulfur-embedded clay-OM aggregates has allowed the imaging of sedimentary carbon that was not previously recognized due to its size or morphology. Traditionally, sedimentary OM was recognized by its morphology. That led to the inevitable overemphasis of polysaccharide networks and underrepresentation of very small (<50 nm) OM masses that tend to be intimately associated with clay mineral aggregates. Because EFTEM can map all carbon, researchers can now study sedimentary OM that does not have recognizable morphology or size.

RELATED PROJECTS

1 – Carla Koretsky (GA Tech), Philippe Van Cappellen (U. Utrecht), Dawn Lavoie (NRL), and I are comparing the deterministic and stochastic approaches to bioirrigation using data from the same mesocosm tanks and St. Louis Bay.

2 – Dawn Lavoie (NRL), Bill Barker (U. Wisconsin-Madison), and I are investigating the optimal sample preparation methods for clay-OM aggregate imaging.

3 – Sam Bentley (LSU) and I are studying the particle transport processes as a function of burrow flushing frequencies, ratio of active to abandoned burrows, and spatial distribution of burrows using the same benthic mesocosm tank platform and field test sites in St. Louis Bay.

4 – Jim Kubicki (Penn State) and I are investigating the spatial relationship between soil mineral aggregates and PAH's using the EFTEM techniques.

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